



## Environmental impact of industrial sludge stabilization/solidification products: Chemical or ecotoxicological hazard evaluation?

Marcos A.R. Silva, Renan C. Testolin, Alcione P. Godinho-Castro, Albertina X.R. Corrêa, Claudemir M. Radetski\*

Universidade do Vale do Itajaí, Laboratório de Remediação Ambiental, Rua Uruguai, 458, Itajaí (SC), Brazil

### ARTICLE INFO

#### Article history:

Received 7 February 2011

Received in revised form 13 May 2011

Accepted 7 June 2011

Available online 14 June 2011

#### Keywords:

Industrial hazardous waste

Environmental impact

Ecotoxicity tests

Stabilization/solidification

Metals

### ABSTRACT

Nowadays, the classification of industrial solid wastes is not based on risk analysis, thus the aim of this study was to compare the toxicity classifications based on the chemical and ecotoxicological characterization of four industrial sludges submitted to a two-step stabilization/solidification (S/S) processes. To classify S/S products as hazardous or non-hazardous, values cited in Brazilian chemical waste regulations were adopted and compared to the results obtained with a battery of biotests (bacteria, alga and daphnids) which were carried out with soluble and leaching fractions. In some cases the hazardous potential of industrial sludge was underestimated, since the S/S products obtained from the metal-mechanics and automotive sludges were chemically classified as non-hazardous (but non-inert) when the ecotoxicity tests showed toxicity values for leaching and soluble fractions. In other cases, the environmental impact was overestimated, since the S/S products of the textile sludges were chemically classified as non-inert (but non-hazardous) while ecotoxicity tests did not reveal any effects on bacteria, daphnids and algae. From the results of the chemical and ecotoxicological analyses we concluded that: (i) current regulations related to solid waste classification based on leachability and solubility tests do not ensure reliable results with respect to environmental protection; (ii) the two-step process was very effective in terms of metal immobilization, even at higher metal-concentrations. Considering that S/S products will be subject to environmental conditions, it is of great interest to test the ecotoxicity potential of the contaminants release from these products with a view to avoiding environmental impact given the unreliability of ecotoxicological estimations originating from chemical analysis.

© 2011 Elsevier B.V. All rights reserved.

### 1. Introduction

In recent years, ecotoxicological tests have become an essential tool to evaluate the environmental impact of chemicals released into the environment, since in these tests the (eco)toxicity of the contaminants is measured, taking into account chemical speciation and bioavailability of contaminants, and synergistic or antagonistic effects of the mixture constituents [1–4]. However, in most regulations worldwide, the (eco)toxicity potential of wastes is derived from classical chemical analysis interpretation, which is used to determine the most appropriate destination or means of disposal for waste material, according to its classification as hazardous/non-hazardous and inert/non-inert properties. In Brazil, federal guidelines classify the hazard status of industrial waste based on the chemical constituents and on leaching and solubility tests [5], similarly to the USA Code of Federal Regulations (CFR Title 40, Part 260–265). Thus, Brazilian waste regulations clas-

sify solid wastes as hazardous (Class I) or non-hazardous (Class II), Class II being split into Class II A (non-inert) and Class II B (inert). In the European Union, the Hazardous Waste Council Directive 91/689/EEC has defined a set of 14 properties allowing waste classification and one of them is the ecotoxicity property (H14), which is defined as substances and preparations which present or may present immediate or delayed risks for one or more sectors of the environment [6]. However, in this directive there is no reference to specific methods for ecotoxicity evaluation. In this context, an experimental test strategy based on a battery of biotests for waste toxicity characterization was published some years ago [7].

On the other hand, the stabilization/solidification (S/S) of sludge originating from wastewater treatment can provide an alternative to waste disposal, and can originate products in a safe and profitable manner. In this regard, technology involving the S/S processes is currently being used to treat a wide variety of wastes containing contaminants such as metals, organic compounds and soluble salts [8–10], but it is most suitable for treating wastes that are predominantly inorganic, as these are considered to be more compatible with the types of cementitious materials normally used [11].

\* Corresponding author. Tel.: +55 47 3341 7970; fax: +55 47 3341 7970.  
E-mail address: [radetski@univali.br](mailto:radetski@univali.br) (C.M. Radetski).

Assessment of the S/S process efficiency is generally carried out by: (i) physical characterization of the S/S products (e.g., compressive strength test) [12]; and/or (ii) solid, leachable and soluble chemical characterization of S/S products (e.g., determination of diffusion coefficients and leachability indices) [13]; and/or (iii) toxicity estimation of the leachable fraction of S/S products (e.g., toxicity characteristic leaching procedure) [14]. Recently, a series of test methods and performance thresholds were proposed for use in the evaluation of the treatability of industrial wastes by S/S, and for the optimization of S/S formulations [15].

Considering that S/S products will be subject to environmental conditions, it is of great interest to measure the ecotoxicity potential of the contaminants released from these products. The results obtained can then be compared with those of chemical analysis to verify the agreement between the two approaches, aiming to protect living organisms. Thus, the aim of this study was to compare the toxicity classification based on the (eco)toxicological and chemical analyses of four industrial sludge samples after submission to the stabilization/solidification (S/S) processes, according to the chemical limits of current Brazilian waste regulation.

## 2. Materials and methods

### 2.1. Sludge source and metal analysis

The industrial sludges used in this study came from two different textile mills, a metal-mechanics plant, and an automotive plant. Metal analysis of the sludge and aqueous samples was carried out according to standard methods [16] and the variability of measured concentrations was presented as the coefficient of variation (CV), which was calculated by dividing the Standard Deviation by the Mean value of the response, multiplied by 100 ( $n=3$ ). Only metals cited in Brazilian chemical waste regulations were analyzed.

### 2.2. Stabilization/solidification treatment

The following experimental design for the stabilization/solidification of the industrial sludge was optimized in a previous study (results not published).

#### 2.2.1. Step 1

The industrial sludge (3 kg-dry weight) was placed in a 20-L mixer. Clay (1 kg) and quicklime (2 kg) were added and the mixture was stirred for 2 h. The quicklime was added 30 min after the clay. After homogenization, the mixture was allowed to stabilize/solidify for 7 days (exothermic phase). Initially, a clod mixture was formed, but after 7 days (end of exothermic phase) a fine powder was obtained. The optimized composition of the components stabilized in Step 1 was quicklime 33.33%, clay 16.66%, and raw sludge 50.00%.

#### 2.2.2. Step 2

The stabilized solid waste product obtained in Step 1 (6 kg) was re-solidified by mixing with Portland cement (4 kg), sand (2 kg), and water (6 L). After homogenization, the concrete block manufactured was allowed to stabilize/solidify for 28 days (curing time) at  $25 \pm 2^\circ\text{C}$  and a relative humidity of  $83 \pm 3\%$ . The Portland cement used was type CPV-ARI (extra strong for use in structures). The optimized composition of the components solidified in Step 2 was cement (22.22%), sand (11.11%), water (33.33%) and stabilized sludge (33.33%).

### 2.3. Leachability and solubility tests

One concrete block was fragmented (sieved at 0.1 mm), homogenized and used to carry out the leachability and solubility tests.

The leachability and solubility tests were carried out according to the Brazilian standard methods [17,18]. In the leachability test, a solid sample (20 g) was placed in a 500 mL bottle and 320 mL of distilled water was added along with a sufficient quantity of acetic acid (80 mL, 0.5 N) to adjust the pH to 5.0. The initial pH was 11.2, which was adjusted under stirring to 5.0, and the final pH was 5.1. The suspension was stirred for 24 h. After filtration with a GF membrane (20  $\mu\text{m}$ ) the leached contaminants were analyzed. In the solubility test, a solid sample size of 25 g was placed in a 500 mL bottle with the addition of 100 mL of distilled water. After 1 h of homogenization, the suspension was allowed to stand for 7 days. After filtration, soluble contaminant concentrations were determined according to the standard methods [16].

### 2.4. Ecotoxicity tests

The ecotoxicity tests were carried out with leachate and soluble fractions of S/S products, i.e., after Step 2 treatment of the different sludges. To carry out these tests, the S/S product fractions were adjusted according to the different standardized protocols applied in the assays.

#### 2.4.1. Algae

The algal species used was *Scenedesmus subspicatus* Chodat (strain 86.81 SAG, Göttingen, Germany). Three algal tests for leachate samples were conducted according to the ISO standardized protocol [19] with three replicates per concentration (or control). Aqueous samples were tested at the following dilutions (%): 3.1; 6.2; 12.5; 25.0; 50.0 and 80.0, i.e., the percentage of leachate or soluble fraction in the dilution tested. Potassium dichromate was used as a positive control. The cell density of the mixture was adjusted to  $10,000 \text{ cells mL}^{-1}$  by dilution with ISO freshwater algal test medium. Each test consisted of seven filtered leachate dilutions and a control group. The test flasks were incubated on a shaker (100 rpm) with continuous illumination of  $70 \mu\text{E m}^{-2} \text{ s}^{-1}$  (cool-white fluorescent lamps) at  $23 \pm 2^\circ\text{C}$ . After 72 h of incubation, the inhibitory effect based on fluorescent activity was measured at  $\lambda = 685 \text{ nm}$  with a Shimadzu RF-551 (Kyoto, Japan) spectrofluorimeter.

#### 2.4.2. Lumistox test

The bacterial (*Vibrio fischeri*) luminescence inhibition (i.e., Lumistox, Dr. Bruno Lange, Düsseldorf, Germany) test was conducted according to ISO guidelines [20] at  $15 \pm 1^\circ\text{C}$  on water samples with salinity adjustment to 35 ppt at pH 7. Aqueous samples were tested at the following dilutions (%): 3.1; 6.2; 12.5; 25.0; 50.0 and 80.0, i.e., the percentage of leaching or soluble fraction in the dilution tested. The exposure time was 30 min. The lyophilized bacterial reagent was obtained from Deutsche Sammlung von Mikroorganismen und Zellkulturen (German Collection of Microorganisms and Cell Cultures) (DSM N# 7151, Braunschweig, Germany). Each dilution sample (or control) was performed in triplicate.

#### 2.4.3. *Daphnia magna* immobility test

The 48-h immobilization test with *Daphnia magna* was performed in accordance with the ISO standard [21] at  $25 \pm 2^\circ\text{C}$  using 5 individuals per replicate (less than 24 h old) in 50-mL glass beakers with 30 mL of test medium. Three different tests (with triplicates) were performed for each sample dilution (or control) in order to evaluate the variability of the procedure. Aqueous samples were tested at the following dilutions (%): 3.1; 6.2; 12.5; 25.0; 50.0 and 80.0, i.e., percentage of leachate or soluble fraction in the dilution tested. Potassium dichromate was used as a positive control.

**Table 1**  
Chemical composition of the raw sludges before application of the stabilization/solidification process. Data are in mg kg<sup>-1</sup> and CV (% in parenthesis).

Parameter	Metal-mechanics sludge	Textile sludge 1	Textile sludge 2	Automotive sludge
Al	9556 (11.3)	14,796 (9.2)	10,976 (8.9)	12,351 (10.1)
As	ND	ND	ND	ND
Ba	49.7 (6.3)	131 (10.5)	ND (1)	91.4 (8.1)
Cd	ND	0.99 (7.4)	ND	ND
Ca	40,688 (12.0)	7645 (11.9)	658 (9.9)	3206 (6.8)
Pb	35.2 (12.8)	56.5 (13.1)	ND	13.7 (10.7)
Cu	19.1 (11.5)	63.0 (12.2)	79.5 (9.8)	48.7 (10.4)
Cr	7.21 (13.2)	50.6 (12.2)	4.87 (13.1)	237 (11.9)
Fe	1257 (5.4)	1839 (9.0)	1929 (7.4)	1911 (10.1)
F <sup>-</sup>	ND	6.67 (5.7)	ND	ND
Mn	42.1 (13.5)	27.7 (15.7)	49.1 (8.9)	24.4 (10.2)
Hg	ND	ND	ND	ND
Ni	ND	5.73 (11.6)	2.60 (12.5)	2.87 (14.2)
pH	9.5 (1.7)	7.2 (1.5)	7.2 (1.3)	5.6 (1.6)
K	42.7 (13.1)	58.7 (6.9)	80.4 (10.4)	30.4 (7.3)
Si	11,238 (14.2)	59,200 (10.8)	4083 (11.9)	5600 (12.3)
Na	262 (4.3)	334 (6.8)	790 (5.2)	268 (6.0)
Zn	174 (12.1)	199 (6.4)	21.0 (10.7)	414 (8.8)
Humidity (%)	41.6 (3.4)	30.6 (6.3)	34.6 (4.4)	26.4 (4.2)

ND – Not detected.

### 2.5. Statistical analysis for ecotoxicity tests

Organism responses were quantified by means ( $X$ ) of 3 independent experiments. The Williams test ( $P \leq 0.05$ ) was used to obtain the lowest-observed-effect concentration (LOEC) after applying Shapiro–Wilk's test for normality and Hartley's test for the homogeneity of variance [22]. The software TOXSTAT 3.0 (University of Wyoming, Laramie, WY) was used for the calculations.

### 3. Results and discussion

Prior to the application of the S/S processes, an initial analysis of the constituents of interest was carried out for the four sludges studied (Table 1).

From the data given in Table 1, all four industrial sludges studied were classified as hazardous wastes according to the Brazilian solid waste regulations [5]. The metal-mechanics sludge was found to contain Pb, Cu and Zn, while textile sludge 1 contained Cd, Cr, Cu, Pb and Ni, and in the textile sludge 2 Cu and Zn were present. The automotive sludge was found to contain Cr, Cu, Pb and Zn. Aluminum appeared in high quantities in all industrial sludges due to coagulant/flocculant agents used in the wastewater treatment stations.

After these initial characterizations, the S/S process was carried out for each of industrial sludge samples. In the first step the clay acts as a metal adsorbent, which is immobilized by quicklime addition [23–26]. In the second step, solidification occurs following the addition of cement [24,27,28]. Tables 2–5 show the results of

**Table 2**  
Soluble and leaching chemical composition of the metal-mechanics sludge before and after the two-step stabilization/solidification process and ecotoxicity results for the three organisms tested.

Parameter	Values obtained in the leaching test (mg L <sup>-1</sup> ; CV)			Regulatory value (mg L <sup>-1</sup> )	Ecotoxicity (LOEC, % dilution)		
	Raw sludge	After Step 1	After Step 2		B	A	D
As	ND	ND	ND	1.0	50	NT	25
Ba	0.22 (8.5)	1.71 (10.3)	0.29 (9.8)	70.0			
Cd	ND	ND	ND	0.5			
Pb	ND	ND	ND	1.0			
Cr	ND	ND	ND	5.0			
F <sup>-</sup>	0.2 (10.1)	1.0 (6.8)	3.1 (12.3)	150.0			
Hg	0.002 (13.1)	ND	ND	0.1			
Ag	ND	ND	ND	5.0			
Se	ND	ND	ND	1.0			

  

Parameter	Values obtained in the solubility test (mg L <sup>-1</sup> ; CV)			Regulatory value (mg L <sup>-1</sup> )	Ecotoxicity (LOEC, % dilution)		
	Raw sludge	After Step 1	After Step 2		B	A	D
Al	59.8 (8.0)	0.20 (10.3)	0.38 (9.5)	0.2	NT	NT	50
As	ND	ND	ND	0.01			
Ba	ND	1.53 (8.2)	1.27 (5.5)	0.7			
Cd	ND	ND	ND	0.005			
Pb	0.46 (9.6)	ND	ND	0.05			
CN <sup>-</sup>	ND	ND	ND	0.07			
Cu	0.67 (8.7)	0.11 (11.2)	ND	2.0			
Cr	ND	ND	ND	0.05			
Fe	0.48 (7.6)	0.05 (10.3)	ND	0.3			
Mn	ND	ND	ND	0.1			
Ag	ND	ND	ND	0.05			
Zn	ND	ND	ND	5.0			

ND – Not detected, B = Bacteria, A = Algae, D = Daphnids, NT – Not Toxic.

**Table 3**

Soluble and leaching chemical composition of textile sludge 1 before and after the two-step stabilization/solidification process and ecotoxicity results for the three organisms tested.

Parameter	Values obtained in the leaching test (mg L <sup>-1</sup> ; CV)			Regulatory value (mg L <sup>-1</sup> )	Ecotoxicity (LOEC, % dilution)		
	Raw sludge	After Step 1	After Step 2		B	A	D
As	ND	ND	ND	1.0	NT	NT	NT
Ba	0.23 (8.4)	3.17 (4.2)	0.43 (9.5)	70.0			
Cd	ND	ND	ND	0.5			
Pb	ND	ND	ND	1.0			
Cr	ND	ND	ND	5.0			
F <sup>-</sup>	0.2 (6.5)	0.9 (8.1)	3.0 (5.0)	150.0			
Hg	ND	ND	ND	0.1			
Ag	ND	ND	ND	5.0			
Se	ND	ND	ND	1.0			

  

Parameter	Values obtained in the solubility test (mg L <sup>-1</sup> ; CV)			Regulatory value (mg L <sup>-1</sup> )	Ecotoxicity (LOEC, % dilution)		
	Raw sludge	After Step 1	After Step 2		B	A	D
Al	ND	0.17 (11.2)	0.41 (9.3)	0.2	NT	NT	NT
As	ND	ND	ND	0.01			
Ba	ND	1.97 (7.7)	1.33 (9.2)	0.7			
Cd	ND	ND	ND	0.005			
Pb	ND	ND	ND	0.05			
CN <sup>-</sup>	ND	ND	ND	0.07			
Cu	ND	0.11	ND	2.0			
Cr	ND	ND	ND	0.05			
Fe	ND	0.09 (5.9)	0.07 (11.3)	0.3			
Mn	ND	ND	ND	0.1			
Ag	ND	ND	ND	0.05			
Zn	0.04 (11.5)	ND	ND	5.0			

ND – Not detected, B = Bacteria, A = Algae, D = Daphnids, NT – Not toxic.

the chemical analysis of the leachable and soluble components of the industrial sludge, as well as the composition of the resultant S/S product after the first and second S/S steps and its leachable and soluble components. The results were compared with the values given in the Brazilian regulations for the classification of solid wastes [5,17,18]. The ecotoxicological profile of each sample is also shown in these tables.

As described above, the values given in Table 1 show that all of these raw industrial sludges must be classified as hazardous wastes according to the Brazilian regulation. However, if we consider the results in Tables 2–5 for the S/S products, the compositions of the leachate and soluble fractions of all S/S products can be classified as non-hazardous and non-inert solid wastes. Barium and aluminum were the parameters responsible for the latter classifica-

**Table 4**

Soluble and leaching chemical composition of the textile sludge 2 before and after the two-step stabilization/solidification process application and ecotoxicity results for the three organisms tested.

Parameter	Values obtained in the leaching test (mg L <sup>-1</sup> ; CV)			Regulatory value (mg L <sup>-1</sup> )	Ecotoxicity (LOEC, % dilution)		
	Raw sludge	After Step 1	After Step 2		B	A	D
As	ND	ND	ND	1.0	NT	NT	NT
Ba	ND	1.37 (10.8)	0.47 (6.9)	70.0			
Cd	ND	ND	ND	0.5			
Pb	ND	ND	ND	1.0			
Cr	ND	ND	ND	5.0			
F <sup>-</sup>	ND	0.8 (11.4)	3.4 (13.5)	150.0			
Hg	ND	ND	ND	0.1			
Ag	ND	ND	ND	5.0			
Se	ND	ND	ND	1.0			

  

Parameter	Values obtained in the solubility test (mg L <sup>-1</sup> ; CV)			Regulatory value (mg L <sup>-1</sup> )	Ecotoxicity (LOEC, % dilution)		
	Raw sludge	After Step 1	After Step 2		B	A	D
Al	9.98 (9.3)	0.06 (14.2)	0.37 (13.2)	0.2	NT	NT	NT
As	ND	ND	ND	0.01			
Ba	ND	0.78 (8.5)	1.56 (11.3)	0.7			
Cd	ND	ND	ND	0.005			
Pb	ND	ND	ND	0.05			
CN <sup>-</sup>	ND	ND	ND	0.07			
Cu	ND	0.72 (10.4)	ND	2.0			
Cr	ND	ND	ND	0.05			
Fe	2.85 (7.0)	ND	ND	0.3			
Mn	0.24 (12.3)	ND	ND	0.1			
Ag	ND	ND	ND	0.05			
Zn	0.26 (8.8)	0.04 (6.9)	ND	5.0			

ND – Not detected, B = Bacteria, A = Algae, D = Daphnids, NT – Not toxic.

**Table 5**  
Soluble and leaching chemical composition of the automotive sludge before and after the two-step stabilization/solidification process application and ecotoxicity results for the three organisms tested.

Parameter	Values obtained in the leaching test (mg L <sup>-1</sup> ; CV)			Regulatory value (mg L <sup>-1</sup> )	Ecotoxicity (LOEC, % dilution)		
	Raw sludge	After Step 1	After Step 2		B	A	D
As	ND	ND	ND	1.0	50	NT	50
Ba	2.87 (8.1)	1.47 (12.2)	0.37 (7.7)	70.0			
Cd	ND	ND	ND	0.5			
Pb	ND	ND	ND	1.0			
Cr	ND	ND	ND	5.0			
F <sup>-</sup>	0.1 (11.6)	1.0 (6.5)	2.5 (9.7)	150.0			
Hg	ND	ND	ND	0.1			
Ag	ND	ND	ND	5.0			
Se	ND	ND	ND	1.0			

  

	Values obtained in the solubility test (mg L <sup>-1</sup> ; CV)			Regulatory value (mg L <sup>-1</sup> )	Ecotoxicity (LOEC, % dilution)		
	Raw sludge	After Step 1	After Step 2		B	A	D
Al	0.18 (13.0)	0.06 (9.2)	0.35 (7.9)	0.2	NT	NT	50
As	ND	ND	ND	0.01			
Ba	4.95 (10.0)	1.56 (6.8)	0.93 (12.3)	0.7			
Cd	ND	ND	ND	0.005			
Pb	ND	ND	ND	0.05			
CN <sup>-</sup>	ND	ND	ND	0.07			
Cu	ND	0.15	ND	2.0			
Cr	ND	ND	ND	0.05			
Fe	108 (12.4)	ND	0.07 (15.2)	0.3			
Mn	4.87 (13.5)	ND	ND	0.1			
Ag	ND	ND	ND	0.05			
Zn	0.16 (13.1)	0.01 (12.6)	ND	5.0			

ND – Not detected, B = Bacteria, A = Algae, D = Daphnids, NT – Not toxic.

tion (Class 2A – non-hazardous and non-inert), but these elements are not considered to be problematic in relation to environmental issues. In other words, Step 1 could be considered as a very efficient stabilization treatment which promotes the immobilization of hazardous metals. In this regard, it is interesting to note that Al was significantly immobilized in Step 1, with the exception of the textile sludge 1, where it was present in a concentration above that found in the raw sludge. For Ba, the comparison of concentrations before and after Step 1 treatment showed a less effective immobilization, since Ba concentrations increased in both chemical tests (exception in the case of automotive sludge). This allowed us to conclude that mobilized barium ions originate from the additional components used in Step 1 and not from the industrial sludge. In this sense, clay used as additional component in Step 1 did not contribute to this metal concentration increment, while leaching and solubility tests with quicklime showed the following values: solubility test = 0.85 mg Al L<sup>-1</sup> and 3.3 mg Ba L<sup>-1</sup>; leaching test = 5.41 mg Ba L<sup>-1</sup>. Nevertheless, it would be useful to perform an additional step to ensure the immobilization of metals, to avoid their physico-chemical alteration in the environment. Analysis of the results for the leachability and solubility of the products generated in Step 2 of the S/S treatment shows that all solidified wastes can be classified as non-hazardous and non-inert, as verified for the wastes stabilized in Step 1.

However, environmental impact from these products must be evaluated to avoid deleterious effects on living organisms exposed to the contaminants released from these products. Thus, the hazardous potential of S/S products was evaluated by ecotoxicity tests representing a primary producer (algae), a primary consumer (daphnids), and a decomposer (bacteria). All important trophic levels of aquatic ecosystems were therefore represented in this study. The results given in Tables 2–5 show that after application of the new S/S process, the S/S products of textile sludges 1 and 2 did not show any ecotoxicity, which allows us to classify them as non-hazardous and non-ecotoxic, despite the limited nature (and number) of the ecotoxicity assays. On the other hand, the S/S product obtained from the automotive sludge cannot be classified as

non-hazardous and non-inert solid waste after application of the new S/S process, since the leachate showed LOEC values of 50% for bacteria and daphnids and the soluble fraction showed a LOEC value of 50% for daphnids. The same ecotoxicity property can be attributed to the metal-mechanics S/S product that showed LOEC values of 50% for bacteria and 25% for daphnids, while the soluble fraction showed a LOEC value of 50% for daphnids. It should be noted that these LOEC values can be considered to indicate low ecotoxicity potential, since not effective concentration values in terms of effects on 50% of exposed populations (EC50) were observed.

Thus, when we compare chemical and ecotoxicological characterization of S/S products, we can conclude that chemical regulation could overestimate or underestimate the hazardous potential of S/S products, which indicates that chemical characterization is not suitable for the evaluation of environmental impact as investigated in this study.

#### 4. Conclusions

Our results showed that current Brazilian (and worldwide) regulations regarding solid waste classifications based on chemical analysis (leachability and solubility tests) is not always appropriate to evaluate the potential environmental impact from solid waste submitted (or not) to the S/S process. In some cases the hazardous potential of industrial sludge was underestimated. The S/S products obtained from the metal-mechanics and automotive sludges were chemically classified as non-hazardous (but non-inert) when the ecotoxicity tests showed toxicity values for leaching and soluble fractions. In other cases, the environmental impact of S/S products was overestimated. The S/S products of the textile sludges were chemically classified as non-inert (but non-hazardous) while ecotoxicity tests did not reveal any effects on bacteria, daphnids and algae. Thus, clay-quicklime stabilization/solidification followed by Portland cement stabilization/solidification was efficient in immobilizing the hazardous heavy metal constituents of textile sludges, since no ecotoxicity effects were observed when the leaching and soluble fractions of S/S products were submitted to a battery of

biotests. For the metal-mechanics and automotive sludges the leaching and/or soluble fractions of S/S products showed a low ecotoxicity toward bacteria and daphnids. If we consider the three ecotoxicity tests performed in this study, the test on *Daphnia magna* was slightly more sensitive than that on the *Vibrio fischeri* bacteria, both of these tests being more sensitive than that on *Scenedesmus subspicatus* algae. Due to the relatively low cost of the S/S processes for the treatment of industrial sludges, together with the possibility for the beneficial use of the immobilized material, this type of treatment appears to offer a promising way to improve environmental quality in many countries. Application of the S/S processes to other industrial inorganic sludges must be subject to efficiency evaluations to avoid the environmental impact of S/S generated products and, in this regard, a battery of ecotoxicity tests must be considered to assess the potential hazardous associated with this practice.

### Acknowledgements

M.A.R. Silva and C.M. Radetski acknowledge fellowships from the Brazilian government funding agency CNPq-Conselho Nacional de Desenvolvimento Científico e Tecnológico (Grant N° 300898/2007-0).

### References

- [1] J.M. Thomas, J.R. Skalski, J.F. Cline, M.C. McShane, W.E. Miller, S.A. Peterson, C.A. Callahan, J.C. Greene, Characterization of chemical waste site contamination and determination of its extent using bioassays, *Environ. Toxicol. Chem.* 5 (1986) 487–501.
- [2] P. Vasseur, J.-F. Féraud, Evaluation de la toxicité des effluents industriels, *Carrefour Sci. Tech.* 1 (1993) 73–75.
- [3] N. Lapa, R. Barbosa, J. Morais, B. Mendes, J. Méhu, J.F. Santos-Oliveira, Ecotoxicological assessment of leachates from MSWI bottom ashes, *Waste Manage.* 22 (2002) 583–593.
- [4] L. Wolska, A. Sagajdakow, A. Kuczyńska, J. Namieśnik, Application of ecotoxicological studies in integrated environmental monitoring: possibilities and problems, *Trends Anal. Chem.* 26 (2007) 332–344.
- [5] ABNT (Associação Brasileira de Normas Técnicas), Resíduos Sólidos-Classificação, NBR 10004, Rio de Janeiro, RJ, Brasil, 2004.
- [6] EEC, Council Directive 91/689/EEC of 12 December 1991 on hazardous waste, *Off. J. Eur. Commun., L, Legis* 377 (1991) 0020–0027 (31/12/1991).
- [7] P. Pandard, J. Devillers, A.-M. Charissou, V. Poulse, M.-J. Jourdain, J.-F. Féraud, C. Grand, A. Bispo, Selecting a battery of bioassays for ecotoxicological characterization of wastes, *Sci. Total Environ.* 363 (2006) 114–125.
- [8] J.R. Conner, S.L. Hoeffner, The history of stabilization/solidification technology, *Crit. Rev. Environ. Sci. Technol.* 28 (1998) 325–396.
- [9] USEPA (United States Environmental Protection Agency), Treatment technologies for site cleanup: annual status report (EPA-542-R-01-004), tenth edition, Office of Solid Waste and Emergency Response, Washington, DC, 2001.
- [10] S. Paria, P.K. Yuet, Solidification-stabilization of organic and inorganic contaminants using Portland cement: a literature review, *Environ. Rev.* 14 (2006) 217–255.
- [11] R. Malviya, R. Chaudhary, Factors affecting hazardous waste solidification/stabilization: a review, *J. Hazard. Mater.* 137 (2006) 267–276.
- [12] J.-C. Morel, A. Pkka, P. Walker, Compressive strength testing of compressed earth blocks, *Constr. Build. Mater.* 21 (2007) 303–309.
- [13] D.H. Moon, D. Dermatas, An evaluation of lead leachability from stabilized/solidified soils under modified semi-dynamic leaching conditions, *Eng. Geol.* 85 (2006) 67–74.
- [14] USEPA (United States Environmental Protection Agency), Toxicity Characteristic Leaching Procedure (TCLP), Test Method 1311-TCLP, Washington, DC, 1992.
- [15] J.A. Stegemann, Q. Zhou, Screening tests for assessing treatability of inorganic industrial wastes by stabilisation/solidification with cement, *J. Hazard. Mater.* 161 (2009) 300–306.
- [16] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, 21st ed., American Public Health Association/American Water Works Association/Water Environmental Federation, Washington, DC, 2006.
- [17] ABNT (Associação Brasileira de Normas Técnicas), Resíduos Sólidos-Teste de Lixiviação, NBR 10005, Rio de Janeiro, RJ, Brasil, 2004.
- [18] ABNT (Associação Brasileira de Normas Técnicas), Resíduos Sólidos-Teste de Solubilização, NBR 10006, Rio de Janeiro, RJ, Brasil, 2004.
- [19] ISO (International Standard Organization), Water Quality-Freshwater Algal Growth Inhibition Test with *Scenedesmus subspicatus* and *Selenastrum capricornutum*. ISO 8692, Geneva, Switzerland, 1990.
- [20] ISO (International Standard Organization), Water Quality: Determination of the Inhibitory Effect of Water Samples on the Light Emission of *Vibrio fischeri* (Luminescent bacteria test). ISO/DIS 11348-1, Geneva, Switzerland, 1998.
- [21] ISO (International Standard Organization), Water Quality-Determination of the Inhibition of the Mobility of *Daphnia magna* Straus (Cladocera, Crustacea). ISO 6341. International Standard Organization, Geneva, Switzerland, 1989.
- [22] D.A. Williams, A test for differences between treatment means when several dose levels are compared with a zero dose control, *Biometrics* 27 (1971) 103–117.
- [23] C.C. Wiles, A review of solidification/stabilization technology, *J. Hazard. Mater.* 14 (1987) 5–21.
- [24] L.T.C. Neder, Tratamento de resíduos industriais perigosos: tecnologia de encapsulamento por complexos argilominerais-CAMs, Tese (Doutorado em Saúde Pública), Faculdade de Saúde Pública, Universidade de São Paulo, São Paulo, Brasil, 1998.
- [25] S.A. Boyd, W.F. Jaynes, B.S. Ross, Immobilization of organic contaminants by organo-clay: application to soil restoration and hazardous waste containment, in: R.A. Baker (Ed.), *Organic Substances and Sediments in Water*, Lewis Publishers, USA, 1991, pp. 181–200.
- [26] H.B. Bradl, Adsorption of heavy metal ions on soils and soils constituents, *J. Colloid Interface Sci.* 277 (2004) 1–18.
- [27] C. Shi, R. Spence, Designing of cement-based formula for solidification/stabilization of hazardous, radioactive, and mixed wastes, *Crit. Rev. Environ. Sci. Technol.* 34 (2004) 391–417.
- [28] J.R. Conner, S.L. Hoeffner, A critical review of stabilization/solidification technology, *Crit. Rev. Environ. Sci. Technol.* 28 (1998) 397–462.